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# Manganese catalyzed chemo-selective synthesis of acyl cyclopentenes: a combined experimental and computational investigation†

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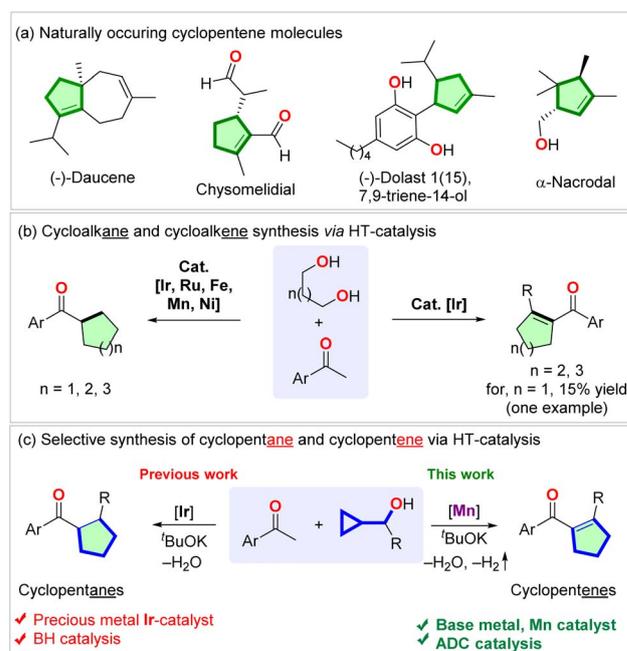
Cyclopentenes serve as foundational structures in numerous natural products and pharmaceuticals. Consequently, the pursuit of innovative synthetic approaches to complement existing protocols is of paramount importance. In this context, we present a novel synthesis route for acyl cyclopentenes through a cascade reaction involving an acceptorless-dehydrogenative coupling of cyclopropyl methanol with methyl ketone, followed by a radical-initiated ring expansion rearrangement of the *in situ* formed vinyl cyclopropenone intermediate. The reaction, catalyzed by an earth-abundant metal complex, occurs under milder conditions, generating water and hydrogen gas as byproducts. Rigorous control experiments and detailed computational studies were conducted to unravel the underlying mechanism. The observed selectivity is explained by entropy-driven alcohol-assisted hydrogen liberation from an Mn-hydride complex, prevailing over the hydrogenation of unsaturated cyclopentenes.

## Introduction

Cyclopentenes are abundant in natural products (Scheme 1a) and are used as pharmaceuticals and medicinal compounds. Because of such importance, the synthesis of cyclopentenes seeks attention.<sup>1–5</sup> Compared to the venerable cyclohexene synthesis *via* the Diels–Alder reaction, the preparation of cyclopentenes *via* [3 + 2] cycloaddition is limited in prominence.<sup>6</sup> The synthesis of cyclopentenes *via* hydrogenation of cyclopentadiene suffers from harsh reaction conditions and poor selectivity due to the uncontrolled over-reduction.<sup>7–9</sup> Other approaches to the synthesis of cyclopentenes *via* ring-closing metathesis needed the synthesis of pre-functionalized alkenes and precious metal catalysts.<sup>10,11</sup> Vinyl cyclopropane rearrangement required multistep starting materials and harsh thermal,<sup>12–14</sup> photochemical,<sup>15,16</sup> or transition metal-catalyzed reaction conditions.<sup>12,16–18</sup> Recently, carbonyl-alkene metathesis<sup>19</sup> and photochemical annulation reactions<sup>6</sup> have also been applied to the synthesis of cyclopentenes. However, the requirement of expensive synthesis of starting materials limits the usefulness of these methodologies. Undoubtedly, intermolecular divergent catalytic protocols utilizing abundant

materials are underdeveloped and are in demand to render new retrosynthesis of these families of carbocycles.

Hydrogen transfer (HT) catalysis has become a versatile tool for waste-free redox transformations.<sup>20,21</sup> Not long ago,



Scheme 1 (a) Selected naturally occurring cyclopentene drug molecules; (b) previous report of the synthesis of cyclopentenes; (c) HT-mediated synthesis of cycloalkanes and cycloalkenes; (d) selective synthesis of cyclopentanes and cyclopentenes *via* HT-catalysis.

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Donohoe, Leitner, Maji, and Adhikary utilized the borrowing hydrogenation (BH) catalysis to synthesize cycloalkanes *via* the annulation of aryl ketones and diols using iridium,<sup>22–24</sup> manganese,<sup>25,26</sup> and nickel<sup>27</sup> catalysts (Scheme 1b, left side). By tuning the ligand and the reaction conditions, the iridium-catalyzed reaction enabled the chemo-selective synthesis of cyclohexenes from pentamethylacetophenone and 1,5-diols (Scheme 1b, right side).<sup>24</sup> However, the same reaction using 1,4-diol gave only 15% yield of one cyclopentene.<sup>24</sup> Recently, Donohoe reported iridium-catalyzed preparation of saturated cyclopentanes (Scheme 1c, left side).<sup>28</sup> However, to our knowledge, the applications of HT catalysis in synthesizing cyclopentenes have not been developed thus far (Scheme 1c, right side).

Employing an earth-abundant metal as a catalyst has an added advantage to sustainable chemical synthesis.<sup>21,29</sup> Manganese complexes have recently been recognized as powerful catalysts for diverse (de)hydrogenation and hydroelementation reactions.<sup>30–32</sup> Particularly, Mn(I)-complexes showed excellent activities in dehydrogenative coupling reactions without needing an acceptor for the liberated hydrogen.<sup>33,34</sup> We are recently intrigued by the possibility of synthesizing multi-substituted acyl cyclopentenes *via* the Mn(I)-complex catalyzed HT-mediated coupling of cyclopropyl methanol with methyl ketone, followed by a single electron transfer (SET)-initiated ring expansion rearrangement of the *in situ* formed vinyl cyclopropenone intermediate (Scheme 1c, right side). We envisioned that by tailoring the catalyst and reaction conditions, it would be possible to facilitate the acceptorless

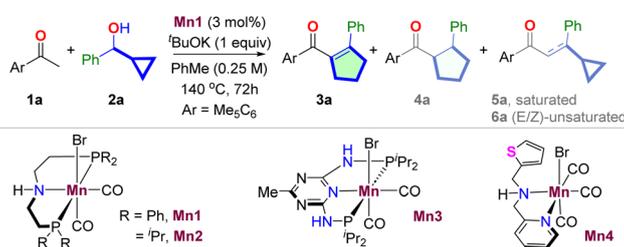
liberation of a hydrogen molecule from a Mn(I)-hydride intermediate before the hydrogenation of the weakly polarized tetrasubstituted alkene could take place. It could thus enable the isolation of these unsaturated compounds, leading to the development of an unprecedented divergent synthesis of cyclopentenes with the generation of water and hydrogen as the byproducts. Herein, we report the realization of the above mechanistic hypothesis. Furthermore, controlled experiments and extensive DFT calculations were performed to understand the reaction mechanism.

## Results and discussion

### Reaction optimization

We began the project by inquiring about the reaction of pentamethyl acetophenone **1a** and 1-phenyl cyclopropyl methanol **2a** for synthesizing acyl cyclopentene **3a** (Table 1, Section S4†). We realized the unique selectivity issue as the HT-mediated cascade of **1a** and **2a** could, together with the desired cyclopentene **3a**, yield saturated cyclopentane **4a**, BH product **5a**, and unrearranged product **6a**. Upon extensive optimization, we have found that the manganese complex **Mn1** derived from the commercially available <sup>Ph</sup>MACHO-ligand produced the desired cyclopentene **3a** in 90% yield in the presence of <sup>t</sup>BuOK in toluene at 140 °C (entry 1). While **4a** was undetected, trace amounts of **5a** and **6a** were observed by gas chromatography. The reaction was found to be sensitive to the bifunctional ligands. The Mn(I)-complexes **Mn2,3** derived from <sup>iPr</sup>MACHO- and PN<sub>3</sub>P-ligands, respectively, provided inferior results (entries

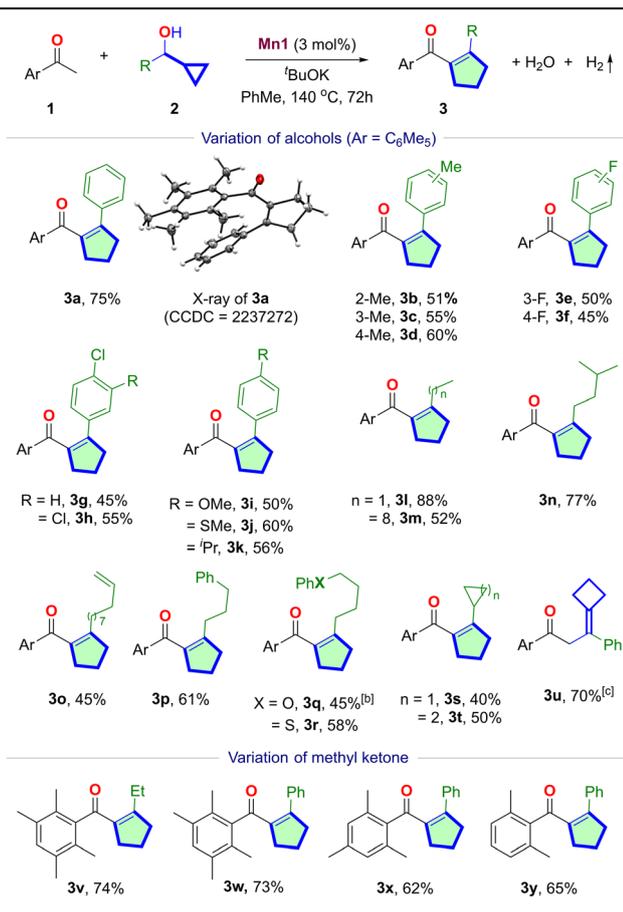
Table 1 Selected reaction optimization<sup>a</sup>



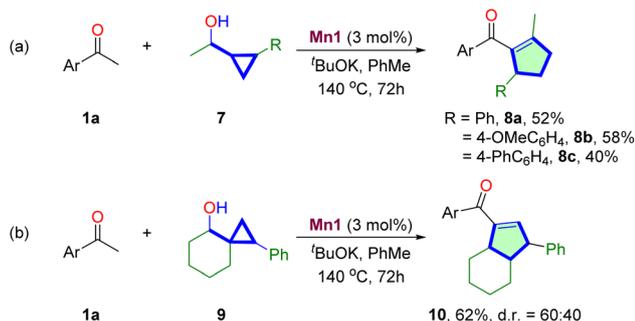
Entry	Deviation from the above	Selectivity <b>1a</b> : <b>3a</b> : <b>4a</b> : <b>5a</b> : <b>6a</b>	% Yield of <b>3a</b>
1	None	2 : 90 : 0 : 5 : 2	90 (75)
2	<b>Mn2</b> instead of <b>Mn1</b>	5 : 51 : 2 : 3 : 0	51
3	<b>Mn3</b> instead of <b>Mn1</b>	8 : 57 : 4 : 2 : 0	57
4	<b>Mn4</b> instead of <b>Mn1</b>	6 : 72 : 22 : 0 : 0	72
5	Na <sup>t</sup> Bu instead of KO <sup>t</sup> Bu	44 : 45 : 0 : 0 : 0	45
6	LiO <sup>t</sup> Bu instead of KO <sup>t</sup> Bu	40 : 20 : 0 : 3 : 0	20
7	KOH instead of KO <sup>t</sup> Bu	55 : 34 : 0 : 2 : 0	34
8	Hexane instead of PhMe	3 : 87 : 4 : 0 : 0	87
9	Dioxane instead of PhMe	4 : 34 : 4 : 0 : 0	34
10	<sup>t</sup> AmOH instead of PhMe	50 : 4 : 0 : 0 : 0	4
11	Without <b>Mn1</b>	100 : 0 : 0 : 0 : 0	0
12	Without KO <sup>t</sup> Bu	100 : 0 : 0 : 0 : 0	0

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), Mn-catalyst (3 mol%), <sup>t</sup>BuOK (1 equiv.), PhMe (0.4 mL), 140 °C, 72 h. Selectivity and yields were calculated *via* gas chromatography using mesitylene as the internal standard. The poor mass balance in some cases is due to the complex, undetected product mixture. Ar=C<sub>6</sub>Me<sub>5</sub>.



Table 2 Substrate scope<sup>a</sup>

<sup>a</sup> Reaction conditions: ketone (0.1 mmol), alcohol (0.2 mmol), **Mn-1** (3 mol%), <sup>t</sup>BuOK (1 equiv.), PhMe (0.4 mL), 140 °C, 72 h. Ar=C<sub>6</sub>Me<sub>5</sub>.  
<sup>b</sup> 0.8 M toluene. <sup>c</sup> With 1-phenyl cyclobutyl methanol **2'**. 0.8 M toluene and 48 h.

Table 3 Reactions with different cyclopropyl rings<sup>3a</sup>

<sup>3a</sup> Reaction conditions: **1a** (0.1 mmol), **7** or **9** (0.2 mmol), Mn-catalyst (3 mol%), <sup>t</sup>BuOK (1 equiv.), PhMe (0.4 mL), 140 °C, 72 h. Ar=C<sub>6</sub>Me<sub>5</sub>.

**2** and **3**). The *N,N*-chelated Mn(i)-complexes **Mn4** that we previously used for cycloalkane synthesis also gave poor results (entry 4).<sup>26</sup> A significant amount of cyclopentane **4a** was formed in the later case. The reaction was also sensitive to the bases used (entries 5–7). <sup>t</sup>BuOK performed better than other bases

tested. Among the solvents, *n*-hexane gave a similar efficiency (entry 9), while others provided poor outcomes (entries 9–10). Control experiments suggested the necessity of each reaction component for successful product formation (entries 11–12).

### Tolerances of the method

With the set of optimized conditions, we explored the scope of Mn(i)-catalyzed cascade cyclopentene synthesis (Table 2). The reaction was minimally affected by the sterics, as *o*-, *m*-, and *p*-tolyl cyclopropylmethanol reacted with **1a** at similar efficiencies, yielding the desired cyclopentenones **3b–3d** in similar yields. The reaction tolerates halogens at different positions of the aryl ring, delivering **3e–3h** in moderate yields. Aryl cyclopropylmethanol containing *p*-OMe, *p*-SMe, and *p*-<sup>t</sup>Pr groups also reacted smoothly, providing the cyclopentenones **3i–3k** in 50–60% yields. In particular, the reaction was equally efficient with the more challenging alkyl cyclopropylmethanols **3l–3s**. 1-Cyclopropylpropan-1-ol provided **3l** in 88% yield. While the increase in the chain length (**3m**) slightly lowered the yield, branching (**3n**) imparted minimal influence. A terminal alkene in **3o** is retained under these hydrogen-liberating conditions. Similar observations were made with phenyl, ether, and thioether-containing substrates **3p–3r**. Interestingly, dicyclopropylmethanol can also yield β-cyclopropyl cyclopentene **3s** in a moderate 40% yield. Similarly, β-cyclobutyl cyclopentene **3t** was synthesized in 50% yield. However, for the 1-phenyl cyclobutyl methanol, we obtained an exocyclic cyclobutyl alkene product **3u**, with 70% yield (Section S4.9†). The structures of **3a** and **3u** were confirmed *via* single-crystal X-ray crystallography.

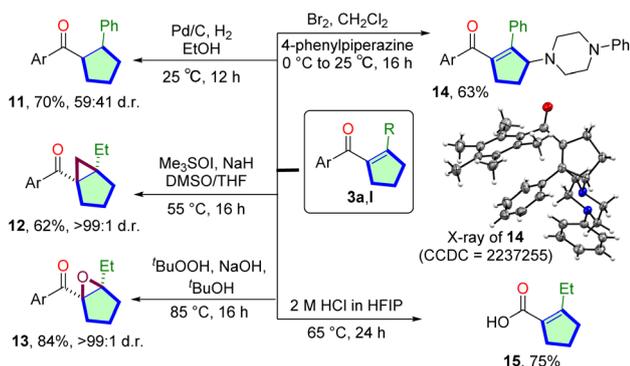
Diverse *ortho*-disubstituted acetophenones can be utilized as the C1-units yielding cyclopentenones **3v–3y** in 62–74% yields. However, when **2a** was treated with acetophenone under standard conditions, a complex mixture resulted, indicating the necessity of *ortho*-substituents that can sterically shield the carbonyl group to slow down reduction and aldol condensations. The advantageous effect of *ortho*-disubstituted methyl ketone has previously been demonstrated.<sup>22</sup>

Then, we were prompted to explore the scope of substituted cyclopropane methanols for synthesizing multisubstituted cyclopentenones (Table 3). The reactions of 1,2-disubstituted cyclopropane methanols **7** with **1a** proceed smoothly to produce 1,2,3-trisubstituted cyclopentenones **8a–8c** in moderate 40–58% yields. The reaction of spiro-bicyclic cyclopropyl alcohol **9** was also investigated. The reaction proceeds at a similar efficiency, producing ring-expanded bicyclic product **10** in 62% yield, albeit in moderate 60 : 40 d.r.

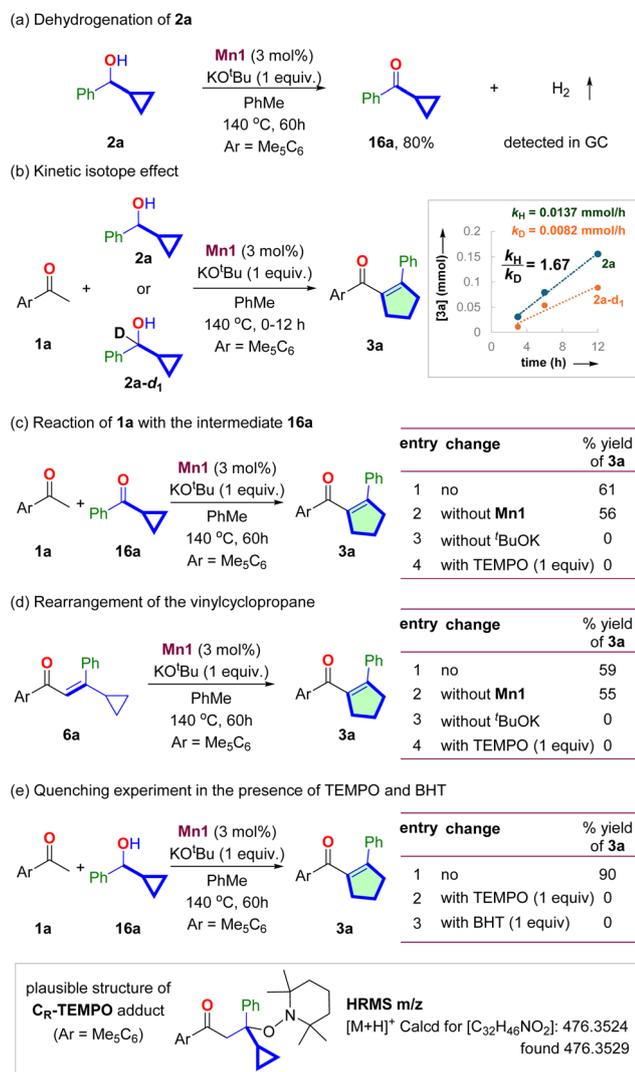
### Synthetic utility

To explore the synthetic utility of the Mn(i)-catalyzed cascade reaction, we have performed derivatization of isolated cyclopentene products (Scheme 2). The Pd/C catalyzed hydrogenation of **3a** and produced the saturated carbocycle **11** in 70% yield. Corey–Chaykovsky cyclopropanation of **3l** delivered bicyclo[3.1.0]hexan-1-yl core **12** in 62% yield and >99 : 1 d.r. We have also conducted the epoxidation of **3l**. The reaction with <sup>t</sup>BuOOH/NaOH produced the tetra-substituted bicyclic epoxide





Scheme 2 Derivatization of the product.

Scheme 3 Mechanistic studies. (a) Dehydrogenation of **2a**, (b) kinetic isotope effect study, (c) reaction of **1a** with **16a**, (d) probing the intermediacy of vinyl cyclopropane, (e) probing the involvement of radicals and plausible structure of the TEMPO adduct.

**13** in a high 84% yield with >99 : 1 d.r. To further functionalize the product, we have performed late-stage  $\gamma$ -amination of **3a** *via* bromine treatment in the presence of piperazine. Allyl amine **14**

was isolated in 63% yield. The molecular structure of **14** was confirmed *via* single-crystal X-ray crystallography.<sup>35</sup> Finally, the pentamethyl aryl group can easily be deprotected *via* retro-Friedel-Craft reactions. The free cyclopentene-1-carboxylic acid **15** was isolated in 75% yield.

### Mechanistic studies and proposed mechanism

The Mn1-catalyzed dehydrogenation of **2a** in the absence of **1a** produced the corresponding ketone **16a** in 80% yield (Scheme 3a, see Section S7.1<sup>†</sup>). The reaction proceeded without an acceptor, and hydrogen gas was detected upon GC analysis of the reaction headspace. The deuterium kinetic isotope effect experiment with **2a** and **2a-d<sub>1</sub>** shows  $k_H/k_D = 1.67$  (Scheme 3b, see Section S7.2<sup>†</sup>). It indicated that the dehydrogenation of secondary cyclopropyl alcohol could be the slowest step of the catalytic cycle. The reaction of **16a** with **1a** under the standard conditions gave 61% yield of product **3a** (Scheme 3c, see Section S7.3<sup>†</sup>). The same reaction without Mn1 also gave a similar yield of **3a**. However, no reaction occurred in the absence of <sup>t</sup>BuOK. It confirms the intermediacy of **16a** and highlights the necessity of the base for the condensation and rearrangement steps.

We then synthesized the vinyl cyclopropane **6a** and performed control experiments to probe its intermediacy (Scheme 3d, Section S7.4<sup>†</sup>). The subjecting of **6a** under standard conditions resulted in 59% yield of **3a** (Scheme 3b, entry 1). The same reaction without Mn1 also provided 55% yield of **3a** (entry 2). However, in the absence of <sup>t</sup>BuOK, **3a** did not form, and 70% of **6a** was recovered as an *E/Z* mixture (entry 3). These experiments suggested that (i) **6a** is an intermediate for this reaction. (ii) Thermal vinyl-cyclopropane rearrangement did not occur at the reaction temperature. (iii) <sup>t</sup>BuOK mediates the rearrangement of **6a** to **3a**.

Notably, the isomerization of **6a** to **3a** stops in the presence of known radical quenchers, such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (entry 4). The reaction of **1a** with **2a** in the presence of TEMPO and butylated hydroxytoluene (BHT) also did not produce **3a** (Scheme 3e, see Section 7.5<sup>†</sup>). A similar observation was also made for the reaction of **16a** with **1a** (Scheme 3c, entry 4). High-resolution mass spectrometric analysis of the reaction mixture detected  $m/z = 476.3529$ , corresponding to a TEMPO adduct with the composition [C<sub>32</sub>H<sub>45</sub>NO<sub>2</sub>], suggesting the involvement of radical species during the rearrangement step (Scheme 3e).

The studied reaction holds promise for an intriguing ring expansion cascade. To provide in-depth insights into the reaction mechanism, we have further investigated the reaction using density functional theory at B3LYP-D3(BJ)/SMD(toluene)/def2-TZVPP (Fig. 1, 2, and Section S8<sup>†</sup>). For simplicity, we have bifurcated the reaction into (a) Mn-catalyzed dehydrogenation (Fig. 1a and b show the reaction mechanism and corresponding energy profile, respectively) and (b) the aldol condensation coupled to the SET cascade rearrangement (Fig. 2 shows the energy profile and structures of stationary states).

We began by investigating the proposed catalytic cycle for the Mn1-catalyzed dehydrogenation of alcohol **2a** to ketone **16a** (Fig. 1a). As anticipated, our computational studies indicate







the intermediacy of <sup>t</sup>BuOH is sluggish at  $\Delta G^\ddagger = 14.7 \text{ kcal mol}^{-1}$ . At this stage, we have explored different possibilities for rearranging **6a** to **3a**, either through radical mediation or nucleophilic attack (Fig. 2, see Section S8† for details). The <sup>t</sup>BuO<sup>−</sup> mediated SET initiation pathway required a  $28.7 \text{ kcal mol}^{-1}$  energetic requirement (**TS**<sub>SET-L-B</sub>, Fig. 2 and S4†). We identify that <sup>t</sup>BuO<sup>−</sup> could execute the deprotonation of an explicit solvent molecule ( $\Delta G^\ddagger = 6.7 \text{ kcal mol}^{-1}$ ) that results in the generation of the tolyl anion that could facilitate the initiation process on **6a** at a SET barrier of  $6.4 \text{ kcal mol}^{-1}$  (**TS**<sub>SET-L</sub>, Fig. 2). Thus, the SET transforms enone **6a** to the enolate radical **C<sub>R</sub>** in an endoergic fashion. Once **C<sub>R</sub>** is formed, it undergoes a step-wise ring opening and ring closer rearrangement process through **TS**<sub>6<sub>R</sub></sub> and **TS**<sub>7<sub>R</sub></sub>, to deliver the enone radical anion **E<sub>R</sub>**, with the intermediacy of the transient radical species **D<sub>R</sub>**. Notably, the radical initiation with the tolyl anion affords the effective barriers of **TS**<sub>6<sub>R</sub></sub> and **TS**<sub>7<sub>R</sub></sub> as  $28.8$  and  $36.3 \text{ kcal mol}^{-1}$ , respectively. This is totally in agreement with the high temperature ( $140 \text{ }^\circ\text{C}$ ) requirement.

However, once **E<sub>R</sub>** is produced *in situ*, it significantly curtails down the kinetic barrier for SET to  $0.9 \text{ kcal mol}^{-1}$ , as well as stabilizing the radical anion intermediate **C<sub>R</sub>** as referenced with **6a** (Fig. 2). Hence, the radical chain propagation by an electron transfer from **E<sub>R</sub>** transforms **6a** to **C<sub>R</sub>** and furnishes the required driving force to develop a  $\beta,\gamma$ -unsaturated 5-membered cyclopentene **F** during the radical chain termination. This is the reason the radical propagation steps, as shown by the black lines in Fig. 2, display a lower transition state barrier **TS**<sub>7<sub>R</sub></sub> ( $23.7 \text{ kcal mol}^{-1}$ ) and overall exothermicity. Thereby, isomerism of **F** leads to the targeted  $\alpha,\beta$ -unsaturated cyclopentene product **3a**. Our study also unfurls the unique role of catalytic electrons in novel cascade reactions and augments the chemical space with the already rich literature on efficient electron-catalyzed reactions.<sup>49</sup>

Once we reach product molecule **3a**, one may fathom **MnH<sub>2</sub>**-mediated hydrogenation of the cyclopentene ring to the saturated product **4a** (Fig. 3 and S5†), as observed previously with the [Ir(cod)Cl]<sub>2</sub>/cataCXiumA catalyst.<sup>28</sup> Here, we propose a step-wise hydride/proton transfer to  $\beta$ -C and carbonyl O-centers, respectively, to generate the corresponding enol intermediate **4a'**, which gets interconverted to **4a**. To initiate the hydrogenation process, **3a** binds to **MnH<sub>2</sub>** through weak C=O $\cdots$ H-N intermolecular H-bonding in **TS**<sub>9</sub> (Fig. 3 and S5†), which catalyzes the initial Mn  $\rightarrow$  C( $\beta$ ) hydride transfer at an energetic barrier of  $19.2 \text{ kcal mol}^{-1}$  followed by a relatively stable intermediate, **MnH-3a**. The consequent proton transfer step occurs (**TS**<sub>10</sub>) at a low energetic requirement to generate the target cyclopentane in an exoergic fashion. Essentially, under the experimental conditions, the transfer hydrogenation cascade mechanism is possible. However, a closer inspection reveals that the alcohol-mediated dehydrogenation of **MnH<sub>2</sub>** is kinetically more facile ( $\Delta\Delta G^\ddagger = 11.1 \text{ kcal mol}^{-1}$ , *via* **TS**<sub>3</sub>) than hydrogenation of **3a** ( $\Delta\Delta G^\ddagger = 19.2 \text{ kcal mol}^{-1}$ , *via* **TS**<sub>9</sub>). The competitive H<sub>2</sub> release mechanism should be favorable entropically and thus rationalize the observation of an unsaturated cyclopentene product **3a** (see Section S8.3†).

## Conclusion

We reported the first example of the synthesis of acyl cyclopentenes *via* coupling cyclopropane methanol and aryl methyl ketones. A manganese complex derived from a commercially available ligand catalyzed the reaction, delivering the products in moderate to high yields with good selectivities. Water and hydrogen gas were produced as the byproducts. The detailed experimental and computational studies elucidated the reaction mechanism that involved multistep manganese-catalyzed acceptorless alcohol dehydrogenation, aldol condensation, and SET-mediated vinyl cyclopropane ring expansion. Facile alcohol-assisted hydrogen liberation over the hydrogenation of enones explains the selectivity for cyclopentene products. Further, we propose an uncharted mechanism of cooperativity between metal/single electron catalysis that we believe could inspire the design of new cascade reactions.

## Data availability

The ESI† includes all experimental details, including optimization of the synthetic method, synthesis, and characterization of all starting materials and products reported in this study, and mechanistic studies. NMR spectra of all products, crystallography, and computation details are included as well.

## Author contributions

KS and BM conceived the project. KS performed experiments, analyzed products, and performed experimental mechanistic studies with input from BM. PB performed the DFT calculations with input from LR. KS and PB wrote the initial draft with input from BM and LR. BM and LR edited the manuscript. BM and LR acquired financial support for the development of this project.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

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